Research Article

Production of biodiesel from Vietnamese waste coffee: biofuel yield, saturation and stability are all elevated compared with conventional coffee biodiesel

Rhodri W. Jenkins[1*], Emrys H. Ellis[1], Emily J. Lewis[1], Michael Paterson[1], Chien Dinh Le,[2] Valeska P. Ting[1] and Christopher J. Chuck[1]

[1] Department of Chemical Engineering, University of Bath, Claverton Down, BA2 7AY
[2] Department of Oil Refining and Petrochemistry, Hanoi University of Mining and Geology, Duc Thang, Bac Tu Liem,
Hanoi, Vietnam

***Correspondence:** Dr Rhodri Jenkins, Department of Chemical Engineering, University of Bath, Claverton Down, BA2 7AY **Email:** R.W.Jenkins@bath.ac.uk

Running Title: Producing biodiesel from Vietnamese waste coffee

Keywords: Biofuels, bioenergy, Vietnam, coffee waste, waste valorisation

Abbreviations: VCS1, Vietnamese coffee sample 1; **VCS2,** Vietnamese coffee sample 2; **VCS3,** Vietnamese coffee sample 3**; CC,** Colombian coffee**; FAME,** fatty acid methyl ester.

Abstract

In this study the suitability of biodiesel produced from spent Vietnamese coffee was examined. Previous work has demonstrated the geographical origin of the coffee beans has little effect on the composition and physical properties of the biodiesel derived from the spent coffee grounds. Vietnamese coffee, however, is roasted in a range of fats and oils to change and enhance certain flavours and as such has a unique fatty acid profile. The oil yield and biodiesel properties of three Vietnamese coffees were assessed and compared to a coffee of more typical composition – Colombian – as well as to more traditional biodiesel feedstocks (rapeseed, sunflower and palm oils). The yield of oil from fresh Vietnamese coffee oil was generally higher (12.0-14.0%) than the Colombian coffee (9.3%), while the oil yield for the spent Vietnamese coffee (9.3-10.4%) was comparable to the spent Colombian coffee grounds (9.5%). The unsaponifiable matter was also affected and was only present in low levels in the Vietnamese coffee (1.9-4.9%) compared to Colombian coffee (30.4% fresh, 21.4% spent). Vietnamese coffee biodiesel was more saturated than the Colombian coffee. Accordingly the biodiesel was more viscous and had a higher pour point than Colombian coffee biodiesel, with properties more akin to palm biodiesel. Vietnamese coffee biodiesel would therefore be a suitable feedstock for local use in Vietnam due to the more suitable climate and compatibility with the palm feedstock that is currently widely used.

Practical applications

In this study, we assessed the variability and suitability of Vietnamese waste coffee as a source of renewable liquid fuel. Vietnam produces 15% of all coffee consumed globally, equating to 1.7 million tonnes annually, and its use provides a relatively pure waste stream that would facilitate its valorisation. It should also be noted that in biodiesel production, the feedstock accounts for >70% of the overall cost. Using a waste resource that is effectively free drastically improves the economic viability of this alternative fuel technology.

Graphical abstract

Spent coffee grounds from Vietnam is demonstrated to be a suitable source of biodiesel

1 Introduction

Biodiesel, the fatty acid methyl esters (FAMEs) obtained *via* the transesterification of triglycerides with methanol, typically represents between 15-25% of annual global biofuel production [1-3]. Approximately 95% of global biodiesel is derived from edible, first generation oils such as palm, rapeseed and soybean [4]. While the technology is well developed there is simply not enough arable land to increase biofuel production to meet global need and alternative feedstocks are being urgently sought.

The cost of the feedstock accounts for >70% of the overall cost of biodiesel production [5]. Thus, second generation triglycerides including waste oils such as cooking oils and animal fats could represent an alternative and more economical route to biofuel production [6]. A further promising waste resource is spent (post-brew) coffee grounds, which are reported to contain between 10-20% of saponifiable lipid, comparable to traditional terrestrial biodiesel feedstocks [7,8]. Approximately 8 million tonnes of coffee grounds are produced each year [9], which represents a relatively pure waste stream that could be used for biofuel production. A number of studies have demonstrated the suitability of coffee biodiesel as a potential fuel feedstock [10-14]. Interestingly while these studies used coffee from various local areas, the fatty acid profile was relatively constant consisting of four major fatty acids; palmitic acid (C16:0, ~35%), stearic acid (C18:0, ~8%), oleic acid (C18:1, ~5%) and linoleic acid (C18:2, ~44%).

Our previous studies have similarly demonstrated that the country of origin had little effect on the lipid profile of the coffee oil produced except when the coffee was sourced from Vietnam. Vietnamese coffee oil was shown to have elevated levels of saturates in comparison to other coffee oil feedstocks [7].

Vietnam is the second largest producer globally, accounting for 15% of global coffee production (Fig. 1).). The coffee production in Vietnam is mainly concentrated in the South, with the province of Dak Lak contributing about 43% of the national coffee produced. Vietnamese coffee is particularly famous for a niche product where the coffee beans have been eaten and partially digested by civet cats, or 'weasels' prior to brewing [15]. In this process the green beans are harvested from the dung and roasted. The digestion process breaks down some of the proteins in the coffee, resulting in a smooth, less bitter flavour. While the vast majority of Vietnamese coffee is not produced in this way, the roasting process in the region has changed in an attempt to replicate 'civet' coffee's characteristic flavour. The major difference is that the beans are roasted in salt, sugar and butter up to 240 °C. This is likely the reason for the difference between the fatty acid profile.

One of the main issues with biodiesel is its oxidative instability due to the relatively facile abstraction of the bisallylic protons present in polyunsaturated fatty acids [16]. The high temperature processing conditions that coffee beans and grounds are subjected to, *i.e.* roasting and brewing, may partially degrade the composition of the fatty acids present and will significantly reduce the level of natural antioxidants in the coffee [17].

In this study, the variability of different Vietnamese coffee biodiesel was assessed, to determine whether the altered fatty acid profile resulted in a suitable biodiesel and how the complex roasting process affected the oxidative stability of the biodiesel produced. The biodiesels from the three Vietnamese coffees were compared to a typical coffee biodiesel and traditional biodiesel feedstocks.

2 Materials and methods

2.1 Materials

The Vietnamese coffee grounds were purchased *via* an online retailer (Weasel Coffees, www.weaselcoffees.com). Three different Vietnamese coffees were investigated, originally purchased from Weasel Coffees. These were Vietnamese coffee sample 1, sold under the brand name "Mr. Phong" (VCS1), Vietnamese coffee sample 2 sold as "Masterpiece coffee" (VCS2) and Vietnamese coffee sample 3 sold as "Café Blend" (VCS3). As a comparison, an alternative coffee of Colombian origin was purchased from a local high-street coffee shop. Rapeseed, sunflower and palm oil were purchased from local retailers. Hexane [high-performance liquid chromatography (HPLC)-grade], sulfuric acid (glacial), methanol (99.5%+), chloroform (99.5%+), d-chloroform (99.9%+) and ethyl acetate (analytical grade) were purchased from Sigma Aldrich, UK and were not purified prior to use.

2.2 Methods

2.2.1 Brewing

Freshly boiled water (1 litre) was added to a French press coffee maker, before the immediate addition of fresh coffee grounds (100 g). The mixture was manually agitated until all the coffee grounds were submerged. The mixture was brewed for exactly 5 minutes before the plunger was depressed and the liquid fraction was poured off. The solid fraction (spent coffee grounds) was separated *via* gravity filtration, and dried in an oven at 65 °C for 24 hours to remove the water.

2.2.2 Lipid extraction

Lipid extraction was carried out according to an adapted method given by Jenkins, *et al.* [7] Coffee grounds were accurately weighed and added to a suitably sized borosilicate glass vessel, before the addition of hexane according to the following equation:

volume of hexane (ml) = 10 × mass of coffee grounds (g) [1]

The mixture was stirred for 3 hours, before being filtered and washed further with hexane (100 mL). The hexane was then removed *in vacuo* to yield a clear brown oil.

2.2.3 Biodiesel production (Transesterification)

The coffee oil (5 g) was accurately measured and added to an excess of methanol (~50 mL) and sulfuric acid (10 wt% in relation to the oil). The mixture was then refluxed for 24 hours. Upon completion, the reaction mixture was filtered to determine the amount of unsaponifiable material produced. To this, distilled water (100 mL) and chloroform (100 mL) were added to solubilize the polar and non-polar components and aid in phase separation. The organic layer was then washed a further three times with distilled water (100 mL) to remove any unreacted methanol, acid catalyst and glycerol. The chloroform was then removed *in vacuo* to yield a clear brown oil. The resulting oil was then analysed *via* nuclear magnetic resonance (^{1}H NMR), according to previous studies [18], to ensure >99% of the glyceride species had reacted.

2.2.4 Oxidative stability testing

The biodiesel sample (10 mL) was held at 110 °C for 6 hours with a constant airflow bubbled through at a rate of 6.67 cm^3 s^{-1}. 0.5 mL aliquots were taken hourly for a total of 6 hours, before analysis *via* ^{1}H NMR.

2.2.5 Biodiesel analysis

2.2.5.1 Composition analysis

The FAME profile of the biodiesel was analysed using an Agilent 5977B gas chromatograph mass spectrometer (GC/MS), equipped with a capillary column (60 m × 0.250 mm internal diameter) coated with a DB-23 ([50% cyanpropyl]-methylpolysiloxane) stationary phase (0.25 μm film thickness) and a He mobile phase (flow rate of 1.2 mL min^{-1}). Approximately 50 mg of the sample was dissolved into 10 mL of ethyl acetate, and 1 μL of each solution was loaded onto the column and preheated to 150 °C. This temperature was held for 5 min, then the sample was heated to 250 °C at a rate of 2 °C min^{-1}, and held for 2 min. NMR spectroscopic measurements were carried out at 25 °C using a Bruker AV300 spectrometer, operating at 400 MHz. Spectra were referenced to the residual $CHCl_3$ peak from the solvent (δ, 7.26 ppm).

2.2.5.2 Bulk physical property analysis

Kinematic viscosities were determined in accordance with ASTM D445. A Canon–Fenske capillary kinematic viscometer was used. Temperature modulation was achieved using a refrigeration/heating unit. Samples within the viscometer were allowed to rest at 40 °C for a minimum of 5 min prior to viscosity measurement to allow for temperature equilibration. The standard error was found to be ±0.100 mm^2 s^{-1} at 40 °C. Pour points of the fuels were determined visually by cooling of 1.5 mL vials of the samples in a low-temperature freezer, with periodic checking to see if the pour point had been surpassed. The samples were allowed to rest at each temperature for a minimum of 60 min to allow for temperature equilibration. Densities were determined gravimetrically by accurately weighting 10 ±0.01 cm^{-3} of sample to an accuracy of ±0.0005 g. A Grant IKA C1 Calorimeter compact bomb calorimeter was used for all energy density analyses, in accordance to DIN 51900.

3 Results & Discussion

3.1 Sample sets

Each type of coffee had a unique combination of coffee beans or is roasted using a distinctive method. VCS1 and VCS2 contained a mixture of Robusta and Arabica beans with 10% of domesticated weasel coffee. The beans were sourced from the Buon Ma Thuot region in the province of Dak Lak. In addition, VCS2 were roasted using a traditional method coating the beans in a mixture of butter and chocolate. VCS3 contained purely peaberry robusta beans and, as such, had a higher caffeine content than VCS1 or VCS2. The extraction efficiency, chemical composition, and properties of the biodiesel obtained was compared to that of coffee beans of more typical composition (Colombian coffee [CC1]), as well as common biodiesel feedstocks (rapeseed, sunflower and palm oils).

3.2 Lipid extraction

Hexane has been demonstrated to be the most suitable solvent for extraction of the oil [11] and was used in this study. Upon extraction of both fresh and spent coffee grounds, the average yield of coffee oil from fresh Vietnamese coffee grounds ranged from 12.0-14.0 wt% (Figure 2). Extracting spent Vietnamese coffee grounds yielded slightly less oil (9.3-10.3 wt%) presumably as small amounts of the lipid were solubilised in the hot brewing process. The overall loss of coffee oil was minimal (between 2-3%). These oil yields were consistent with those in the literature [13]. Little difference was seen between lipid yields of VCS1, VCS2 and VCS3.

The coffee of Colombian origin (CC1), however, showed lower levels of extracted coffee, with 9.3 wt% for fresh and 9.5 wt% for spent. This is likely due to the process of Vietnamese coffee roasting which adds oils and fats and therefore increases the overall available lipid for extraction. Roasting the beans in oil and butter leads to a significant amount of oil on the surface of the resultant grounds, rather than within the grounds themselves. This would result in the greater lipid yields from the fresh coffee grounds. Loss of this excess surface lipid in the brewing process would also explain the reduction in oil yield from Vietnamese coffee after brewing, while very little difference is seen between the fresh and spent Colombian coffee. This was also consistent with observations of the oils when purified *in vacuo* and allowed to cool to room temperature. A portion of each Vietnamese coffee oil solidified leading to a two-

phase product, likely caused by the saturates present in butter and cocoa lipids, while the CC1 oil remained as a liquid (see supporting information).

3.3 Transesterification / Unsaponifiables

After extraction, the coffee oil was transesterified using an excess of methanol and sulfuric acid as a catalyst. This method produced a blue-black solid unsaponifiable material [7]. The unsaponifiable material was seperated from the reaction mixture through gravity filtration once the reaction period was complete, the biodiesel was isolated using hexane and washed with distilled water to remove any traces of unreacted material, co-products and catalyst, before being dried *in vacuo* (Fig. 3). The CC1 oil contained more unsaponifiable material (30.3 wt% fresh; 21.39 wt% spent) than the Vietnamese coffee samples (2.2-4.9 wt% fresh; 1.8-4.8 wt% spent). While this will in part be due to the presence of non-coffee lipids in the Vietnamese coffee samples, leading to a reduction in the proportion of unsaponifiable lipids present, it might also be a characteristic of Vietnamese coffee in general. For both coffee types however, brewing led to a reduction in unsaponifiable material, as presumably much of this material is extracted in the brewing process.

The lack of unsaponifiable material in Vietnamese coffee is supported by the ^{1}H NMR analysis of the oils extracted (see supporting information). Typical unsaponifiable sterols present in coffee oil are kahweol and cafestol [19], which are observed in the ^{1}H NMR of the CC1 oil, though entirely lacking in the spectra of the three Vietnamese coffee oils.

3.4 FAME profile

The FAME profile of a biodiesel determines the physical properties of the fuel produced. The FAME profile of the coffee biodiesel was analysed by GC-MS and compared to more common biodiesel feedstocks (Table 1). As expected, the CC1 FAME profile varied little from previously reported values containing methyl palmitate (C16:0, 37%) and methyl linoleate (C18:2, 46%), methyl stearate (C18:0, 8%) and methyl oleate (C18:1, 8%) as well as small amounts (~1%) of methyl linolenate (C18:3) and methyl arachidate (C20:0) [7].

The three Vietnamese coffee biodiesels, however, possessed significantly different FAME profiles to the other coffee biodiesels, with significantly higher amounts of methyl oleate (C18:1, 24.7-26.5%), and lower amounts of methyl linoleate (C18:2, 23.1-26.3%). The lack of variation between the three Vietnamese coffees shows that the different processing methods used within Vietnam have little effect on the overall fatty acid profile. Also present in the Vietnamese coffee biodiesel were small amounts (2.3-5.3%) of methyl laurate (C12:0), typically found in butter and cocoa bean oils. The greater proportions of saturated and monounsaturated FAMEs, as well as the lower levels of polunsaturated FAMEs will have a significant impact on the physical properties of the oil and subsequent biodiesel produced.

3.5 Fuel properties

To assess the suitablity of Vietnamese coffee biodiesel, a number of fuel properties were examined and compared to biodiesel produced from rapeseed, sunflower and palm oils. These have largely differing FAME profiles. Palm biodiesel had fairly equal proportions of saturates (50.7%) and unsaturates (49.4%), while rapeseed and sunflower possessed much higher amounts of total unsaturates, with 92.6% and 89.6% respectively.

3.5.1 Kinematic viscosity

The kinematic viscosty is a measure of flow resistance, and is one of the most important aspects of a fuel as it affects its handling, pumping and atomisation. The international standards for biodiesel specification state that the viscosity of biodiesel (at 40°C) must be between 3.5-5.0 $mm^2\ s^{-1}$ in the EU (EN 14214) [20], or between 1.9-6.0 $mm^2\ s^{-1}$ in the US (ASTM D6751) [21]. The three Vietnamese coffees all exhibited similar viscosities to one another with the fresh samples having a viscosity between 3.30-3.96 $mm^2\ s^{-1}$ which rose to 4.23-4.32 $mm^2\ s^{-1}$ for the spent coffee fuels (Fig. 4). Presumably this is due to the extraction of small amounts of water-soluble biomolecules during the brewing process, which interupt the stacking of the linear fatty acid chains. The viscosity of the Colombian coffee biodiesel descreased slightly upon brewing (from 3.70 to 3.36 $mm^2\ s^{-1}$). The signficantly lower viscosity of the spent CC1 biodiesel, however, is likely due to the higher

proportion of polyunsaturates present. Rapeseed and sunflower biodiesels had similar viscosities of 3.83 and 3.86 $mm^2\ s^{-1}$ while due to the higher saturated profile the palm biodiesel had a far high viscosity (4.35 $mm^2\ s^{-1}$). The Vietnamese coffee biodiesel was far more more similar to the palm-derived biodiesel than other biodiesels examined.

Despite the wide variation in viscosity, all biodiesels produced fell within the US standard for biodiesel, and most fell within the EU standard. The exceptions, fresh VCS2 and spent CC1, exhibited viscosities of 3.30 and 3.36 $mm^2\ s^{-1,}$ respectively, which falls below the EU standard minimum of 3.5 $mm^2\ s^{-1}$. While this is narrowly out of specification it should be noted that the European standard for diesel (EN 590) which can include upto 7% of biodiesel outlines the required viscosity be within 2.0 and 4.5 $mm^2\ s^{-1}$ [22].

3.5.2 Pour point

The pour point of a fuel is the lowest temperature at which the fuel flows before gelling. Operating an engine below a fuel's pour point therefore causes major operability issues. Biodiesel typically has a higher pour point than its petrodiesel counterpart, and therefore cannot be used in high blends at low temperatures.

Little difference was observed between the Vietnamese and Colombian derived coffee biodiesels, though the pour points of the biodiesel obtained from fresh and spent Vietnamese and Colombian coffee exhibited some variation, between 3.0 and 7.5 °C (Fig. 5). There is no clear trend between the effect of brewing, or the different treatment techniques of the Vietnamese coffees. Again, however, the Vietnamese coffee biodiesel was far more similar to palm oil biodiesel (9.5 °C) than either rapeseed (-15.5 °C) or sunflower (-5 °C). The slightly reduced pour points between the coffee and palm fuels could be due to the presence of alternative biomolecules which inhibit sufficient stacking of the fatty acid chains, or the higher proportion of polyunsaturates in the coffee biodiesel.

While the pour points of the biodiesel derived from coffee are not suitable for use in cold climates, they are could be used locally in Vietnam, as well as other regions that rely on palm biodiesel currently.

3.5.3 Energy density

The energy density, or calorific value, is the energy obtainable from a fuel *via* combustion per unit mass, and therefore fuels of varying energy density alter the vehicle range achievable. Biodiesel typically possesses a lower energy density than traditional hydrocarbon based fuels (roughly 10-12% lower) due to the presence of oxygen in its molecular structure. While there is no specific energy density requirement outlined in either European or US standards, a higher energy density is desirable and petrodiesel has a typical energy density of 45 MJ kg^{-1}.

The energy densities of the biodiesel obtained from fresh and spent Vietnamese and Colombian coffee showed some significant variation, with most falling between 35.0 to 38.0 MJ kg^{-1} (Fig. 6), with the exception of VCS2 fresh coffee biodiesel, which possesses a significantly lower energy density (32.0 MJ kg^{-1}). All the spent coffee biodiesel was similar to the other standard rapeseed, palm and sunflower biodiesels, with just the fresh coffee biodiesel differing significantly. Again, this is most likely due to the presence of alterantive oxygenated biomolecules that are removed on brewing.

3.5.4 Nitrogen content

Caffeine is a xanthine based alkaloid containing four nitrogen atoms. Caffeine was found to be present (via ^1H NMR) in all the biodiesels extracted from the fresh coffees, whether Vietnamese or Colombian, though was not observed in biodiesel derived from the spent coffees (See supplementary information). The presence of nitrogen-containing compoounds will, upon combustion, produce harmful mono-nitrogen oxides (NO_x) which are potent greenhouses gases and contribute to smog formation.

The amount of caffeine present can be calculated from the ^1H NMR spectroscopy, using the integration values for the FAME methoxy group (δ 3.6 ppm) and the shift for the aromatic proton in caffeine's structure (δ 7.45 ppm). For the VCS1 fresh coffee oil, the approximate amount of caffeine present is 2.5 mol%. Caffeine would therefore account for 1.6 % of the weight of the fuel, or 21.5 g L^{-1}.

Current European standards quote the emission limits of a car in g km^{-1}. Assuming an average

fuel consumption of a diesel car of 4.5 litres per 100km (combined fuel consumption of a 2014 Ford Focus 1.6 l TDCi), 0.045 litres of fuel would be combusted each km, in which 0.648 g of caffeine would be present. Assuming complete combustion of the caffeine, and that an even amount of NO and NO_2 are produced, this would equate to 0.507 g of NO_x per km. The current European legislation on emissions, Euro 6, allows only 0.080 g km^{-1} NO_x. Irrespective of the level of NO_x produced from atmospheric nitrogen, caffeinated fuels would not be permissible in the EU. It is therefore necessary for coffee biodiesel to be solely produced from used coffee grounds and not from rejected beans or FCG.

3.5.5 Oxidative stability

Oxidative stability is a key factor to consider when storing biodiesel. If the oxidative stability of the biodiesel is poor it will degrade during storage. This can lead to solid deposits and the formation of contaminants including alcohols and acids, and these in turn can have a damaging effect on the engine of a vehicle. Research has shown that biodiesel is less stable than regular diesel due to an increased proportion of unsaturated molecules [23]. The stability of the biodiesel can be affected by many different parameters, including the composition, oxygen content and the presence of antioxidants. The composition of the biodiesel is one the most important factors, as different bond types will be more prone to oxidation than others. The methyl group situated at allyic positions to the double bonds will be the first to be oxidised, and these will further trigger the cyclic reaction due to the formation of hydrogen peroxide ions [24].

All of the samples were held at 110 °C under a constant airflow and the mixture sampled regularly. The samples were analysed by ^1H NMR and the decrease in the number of bisallyic, olefinic and allyic groups present in the biodiesel was assessed according to literature methods (Fig. 7) [25]. There was little degradation observed over this time period for the fresh Vietnamese coffee samples, however the spent Vietnamese coffee biodiesel had significantly degraded over the 6 hour period. It seems likely that the proportion of antioxidants was reduced significantly upon brewing. Coffee is known to contain many different antioxidants including, chlorogenic acids, caffeine, niacin and tocopherols, most of which are removed during the brewing process [26]. In comparison, both the fresh and spent Coloumbian coffee started to degrade under these accelerated conditions. The fresh coffee biodiesel started to degrade after two hours whereas the spent coffee degraded immediately. This demonstrates that the spent coffee biodiesel is more unstable than the fresh, though the standard Colombian coffee had a far lower stability than the Vietnamese biodiesel. This is presumably due to the lower proportions of polyunsaturates in the Vietnamese coffee samples, though the unique roasting method of Vietnamese coffee may introduce other macromolecules such as antioxidants into the biodiesel, which increase its stability.

All of the standard biodiesel samples were stable throughout this testing. Although the rapeseed contains a very large proportion of unsaturated molecules (96%) the majority of these are in the form of 18:1 (69%), the most stable form of unsaturation. Palm oil has a larger proportion of saturation (49%), which is likely to be the cause of its stability especially where (40%) is 18:1. However, this elevated stability is presumably due to the level of antioxidants in the lipid, and it seems likely that coffee biodiesel would need additional additives to increase the stability to an acceptable level.

4 Conclusions

Vietnamese coffee was assessed for its suitability as a biodiesel feedstock in terms of its lipid content, as well as the physical fuel propeties of the biodiesel produced. The level of oil extracted was slightly higher for Vietnamese coffee than for the alternative coffee (Colombian). The FAME profile of the Vietnamese was significantly different from the Colombian (which included an increase in the amount of monounsaturates, and a decrease in polyunsatures), while also including a small number of shorter fatty acids not typically found in coffee oil. These saturates had a large effect on the fuel properties, and the Vietnamese coffee biodiesel was far more similar to palm biodiesel than any other type of biodiesel. Vietnamese coffee offers an attractive source of biodiesel that could be utilised locally. Three alternative types of Vietnamese coffee were assessed and no significant difference was found between them, suggesting that waste

coffee biodiesel sourced from Vietnam would have consistent and predictable fuel properties.

The authors would like to thank the RAEng for partially funding this work through a Newton Fellowship grant (NRCP/1415/176) and to Roger and Sue Whorrod for funding the external fellowship held by CJC.

The authors have declared no conflict of interest.

References

[1] G. Knothe, J. H. V. Gerpen, J. Krahl: The biodiesel handbook. AOCS Press 2005.

[2] The State of Food and Agriculture: Biofuels: Prospects, Risks and Oppurtunities, Food and Agriculture Organization of the United Nations, Rome 2008.

[3] REN21: Renewables 2014: Global status report, 2014.

[4] A. E. Atabani, A. S. Silitonga, I. A. Badruddin, T. M. I. Mahlia, H. H. Masjuki, S. Mekhilef: A comprehensive review on biodiesel as an alternative energy resource and its characteristics, Renewable and Sustainable Energy Reviews. 2012, 16, 2070-2093.

[5] A. Chhetri, K. Watts, M. Islam: Waste Cooking Oil as an Alternate Feedstock for Biodiesel Production, Energies. 2008, 1, 3.

[6] I. B. Banković-Ilić, I. J. Stojković, O. S. Stamenković, V. B. Veljkovic, Y.-T. Hung: Waste animal fats as feedstocks for biodiesel production, Renewable and Sustainable Energy Reviews. 2014, 32, 238-254.

[7] R. W. Jenkins, N. E. Stageman, C. M. Fortune, C. J. Chuck: Effect of the Type of Bean, Processing, and Geographical Location on the Biodiesel Produced from Waste Coffee Grounds, Energy & Fuels. 2014, 28, 1166-1174.

[8] A. Karmakar, S. Karmakar, S. Mukherjee: Properties of various plants and animals feedstocks for biodiesel production, Bioresource Technology. 2010, 101, 7201-7210.

[9] S. Obruca, P. Benesova, S. Petrik, D. Kucera, I. Marova: Biotechnological conversion of spent coffee grounds into polyhydroxyalkanoates, New Biotechnology. 2014, 31, S39-S40.

[10] L. S. Oliveira, A. S. Franca, R. R. S. Camargos, V. P. Ferraz: Coffee oil as a potential feedstock for biodiesel production, Bioresource Technology. 2008, 99, 3244-3250.

[11] Z. Al-Hamamre, S. Foerster, F. Hartmann, M. Kröger, M. Kaltschmitt: Oil extracted from spent coffee grounds as a renewable source for fatty acid methyl ester manufacturing, Fuel. 2012, 96, 70-76.

[12] E. E. Kwon, H. Yi, Y. J. Jeon: Sequential co-production of biodiesel and bioethanol with spent coffee grounds, Bioresource Technology. 2013, 136, 475-480.

[13] D. R. Vardon, B. R. Moser, W. Zheng, K. Witkin, R. L. Evangelista, T. J. Strathmann, K. Rajagopalan, B. K. Sharma: Complete Utilization of Spent Coffee Grounds To Produce Biodiesel, Bio-Oil, and Biochar, Acs Sustainable Chemistry & Engineering. 2013, 1, 1286-1294.

[14] N. S. Caetano, V. F. M. Silva, A. C. Melo, A. A. Martins, T. M. Mata: Spent coffee grounds for biodiesel production and other applications, Clean Technologies and Environmental Policy. 2014, 16, 1423-1430.

[15] B. M. Thout: Coffee in Vietnam: It's the shit, in: The Economist 2012.

[16] C. J. Chuck, C. D. Bannister, R. W. Jenkins, J. P. Lowe, M. G. Davidson: A comparison of analytical techniques and the products formed during the decomposition of biodiesel under accelerated conditions, Fuel. 2012, 96, 426-433.

[17] G. Budryn, E. Nebesny, D. Żyżelewicz, J. Oracz, K. Miśkiewicz, J. Rosicka-Kaczmarek: Influence of roasting conditions on fatty acids and oxidative changes of Robusta coffee oil, European Journal of Lipid Science and Technology. 2012, 114, 1052-1061.

[18] L. A. Anderson, A. K. Franz: Real-Time Monitoring of Transesterification by H-1 NMR Spectroscopy: Catalyst Comparison and Improved Calculation for Biodiesel Conversion, Energy & Fuels. 2012, 26, 6404-6410.

[19] N. D'Amelio, E. De Angelis, L. Navarini, E. Schievano, S. Mammi: Green coffee oil analysis by high-resolution nuclear magnetic resonance spectroscopy, Talanta. 2013, 110, 118-127.

[20] EN 14214: Automotive fuels - Fatty acid methyl esters (FAME) for diesel engines - Requirements and test methods.

[21] ASTM D6751: Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, ASTM International 2008.

[22] EN 590: Automotive fuels - Diesel - Requirements and test methods.

[23] C. Bannister, C. Chuck, M. Bounds, J. Hawley: Oxidative stability of biodiesel fuel, Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering. 2011, 225, 99-114.

[24] C. J. Chuck, R. W. Jenkins, C. D. Bannister, L. Han, J. P. Lowe: Design and preliminary results of an NMR tube reactor to study the oxidative degradation of fatty acid methyl ester, Biomass and Bioenergy. 2012, 47, 188-194.

[25] C. J. Chuck, C. D. Bannister, R. W. Jenkins, J. Lowe, M. G. Davidson: A comparison of analytical techniques and the products formed during the decomposition of biodiesel under accelerated conditions, Fuel. 2012, 96, 426-433.

[26] Y. F. Chu, Coffee: Emerging Health Effects and Disease Prevention. Wiley 2012.

[27] Food and Agriculture Organization of the United Nations: FAOSTAT - Green Coffee World Production Quanttity, 2012.

[28] Trade Statistics (Total Production exporting countries), International Coffee Organization 2015.

--

Tables

Table 1. Mass percent FAME present in the biodiesel produced from extracted coffee oils, and common biodiesel feedstocks used for comparisons in structure and physical properties in this study

FAME	Coffee Oil Biodiesel								Comparisons		
	VCS1		VCS2		VCS3		CC1		Palm	Rapeseed	Sunflower
	Fresh	Spent	Fresh	Spent	Fresh	Spent	Fresh	Spent			
12:0	4.6%	4.6%	4.8%	5.3%	2.3%	4.6%	0.0%	0.0%	0.0%	0.0%	0.0%
16:0	38.4%	37.8%	39.0%	38.4%	39.9%	38.2%	35.0%	35.0%	44.4%	5.1%	6.6%
18:0	5.8%	5.5%	5.6%	5.5%	5.8%	5.5%	7.3%	7.0%	4.6%	1.7%	3.8%
18:1	25.5%	25.9%	25.1%	26.6%	24.7%	25.3%	8.6%	8.5%	39.8%	64.1%	28.5%
18:2	24.4%	24.9%	24.2%	23.1%	26.3%	25.1%	45.1%	45.5%	10.6%	20.0%	60.9%
18:3	0.3%	0.2%	0.3%	0.1%	0.9%	0.1%	1.5%	1.6%	0.3%	8.5%	0.2%
20:0	1.0%	1.1%	0.9%	1.0%	0.1%	1.2%	2.5%	2.3%	0.4%	0.6%	0.0%
Saturates	49.8%	49.0%	50.3%	50.2%	48.1%	49.5%	44.8%	44.3%	49.4%	7.4%	10.4%
Monounsaturates	25.5%	25.9%	25.1%	26.6%	24.7%	25.3%	8.6%	8.5%	39.8%	64.1%	28.5%
Polyunsaturates	24.7%	25.1%	24.5%	23.2%	27.2%	25.2%	46.6%	47.1%	10.9%	28.5%	61.1%
Total unsaturates	50.2%	51.0%	49.6%	49.8%	51.9%	50.5%	55.2%	55.6%	50.7%	92.6%	89.6%

Figures

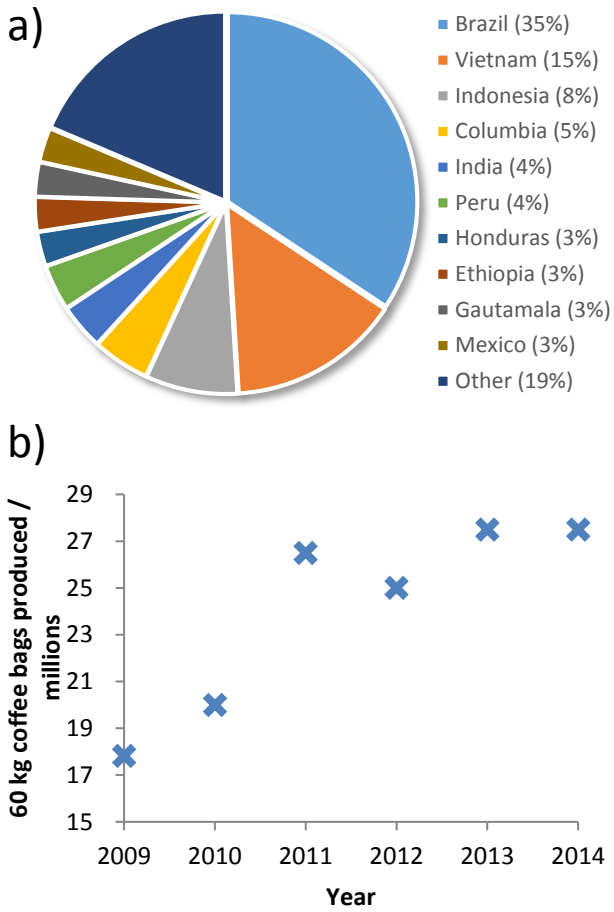

Figure 1. a) Total production of green coffee beans in 2012, adapted from data from the UN Food and Agricultural Organization [27], and; b) Annual coffee production in Vietnam, adapted from data from the International Coffee Organization [28].

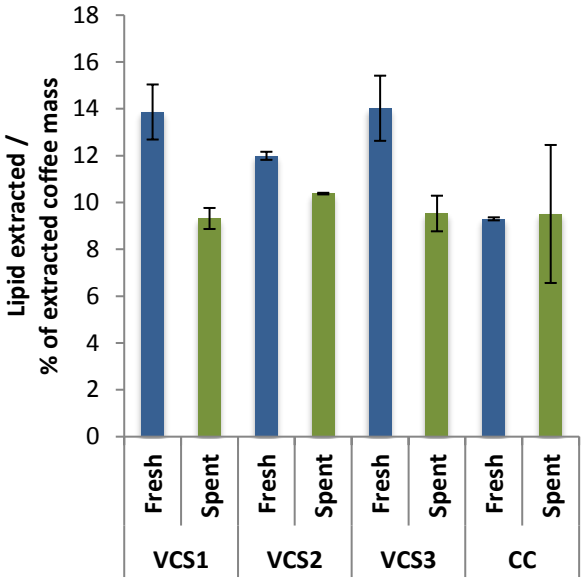

Figure 2. Lipid extraction (by percentage of extracted coffee mass) of different coffees.

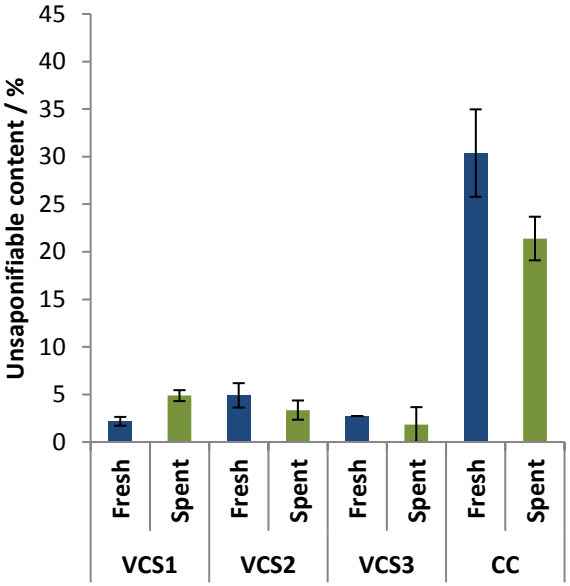

Figure 3. Unsaponifiable content (by percentage of the mass of coffee oil transesterified) of the different coffees assessed.

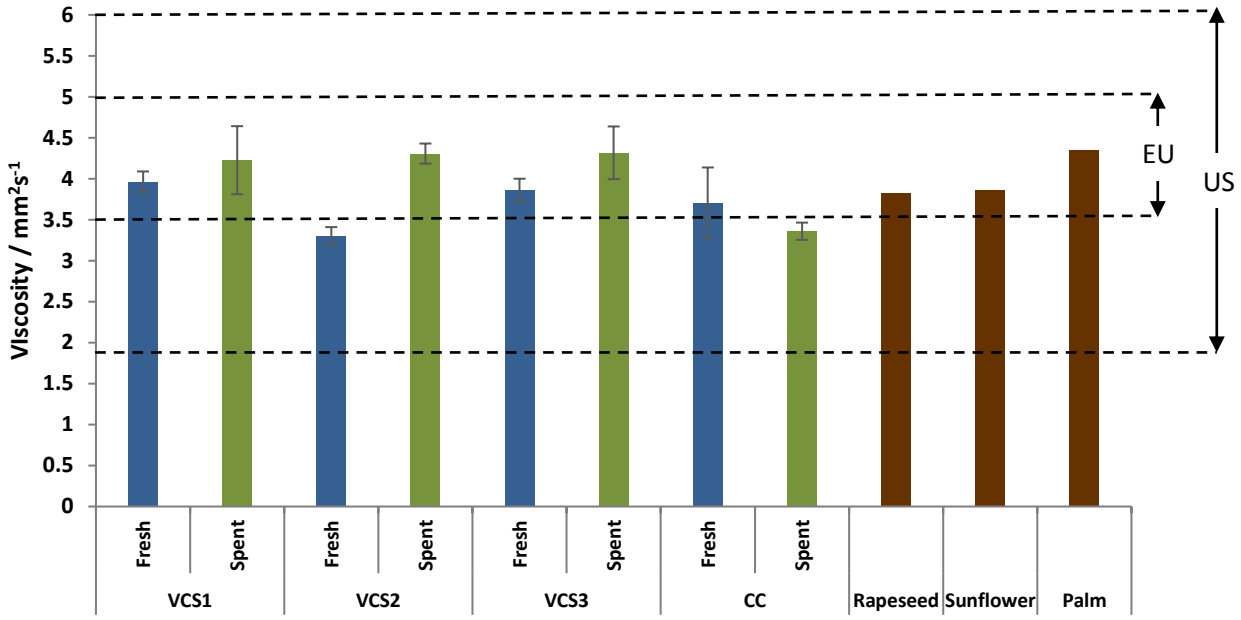

Figure 4. Kinematic viscosity (at 40°C) of the FAME produced from different coffee sources (both fresh and spent), and traditional biodiesel sources, showing the allowed ranges for biodiesel in both EU and US fuel specifications.

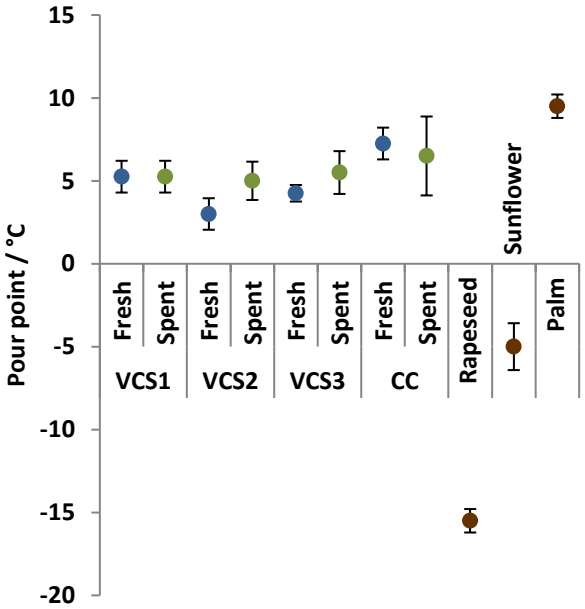

Figure 5. Pour point of the FAME produced from different coffee sources (both fresh and spent), and traditional biodiesel sources.

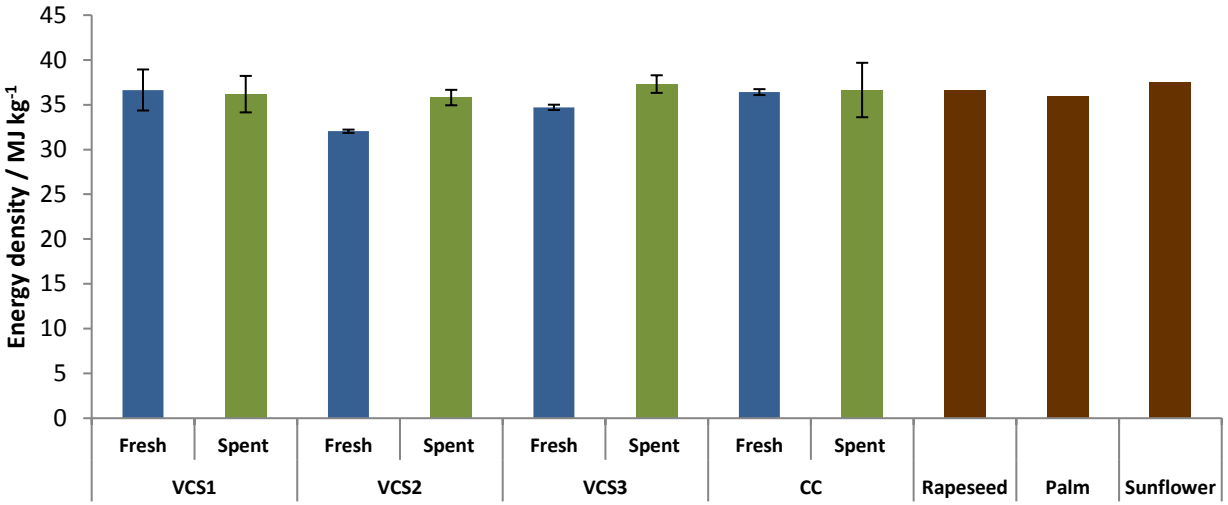

Figure 6. Energy densities of the FAME produced from different coffee sources (both fresh and spent), along with traditional biodiesel sources.

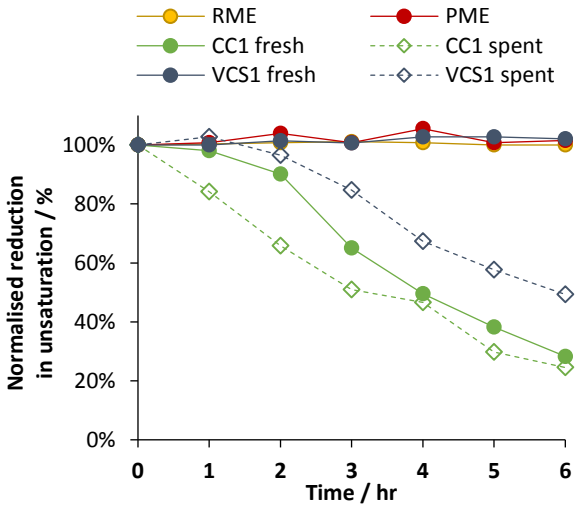

Figure 7. Normalised reduction in unsaturation calculated from the ^{1}H NMR of the biodiesel samples held at 110 °C under a constant airflow

--